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**Solvent Dyeing of Wool with a  
Reactive Dye/Surfactant Complex**

**by**

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# SOLVENT DYEING OF WOOL WITH A REACTIVE DYE/SURFACTANT COMPLEX

by H.D. MEISSNER and B.A. McIVER

## ABSTRACT

*A method is described for dyeing wool with reactive dyes from perchloroethylene utilising the solvent-soluble complex of the dye and a surface-active agent of opposite charge. It requires the addition of a suitable fibre-swelling agent, for which purpose water, and to a limited extent also ethylene glycol, proved useful.*

## KEY WORDS

Perchloroethylene – ethylene glycol – water – hexadecylpyridinium chloride – hexadecylammonium chloride – solvent dyeing – wool – reactive dyes.

## INTRODUCTION

The advantages of dyeing wool from organic solvents compared with aqueous dyeing, have been summarised in a recent paper (1). The various attempts to establish a suitable solvent dyeing process have, however, left some unsolved problems. These seem to arise primarily from the fact that the majority of the existing wool dyes are highly sulphonated and thus insoluble in organic solvents. Dye solutions have therefore to be made up with the aid of polar co-solvents and these in turn emulsified into the organic solvent. As co-solvents, water (2), polyhydric alcohols (3) and mixtures of both (4) have been used, but apart from the fact that dyeing from emulsions is generally likely to produce uneven results, there are other drawbacks such as the existence of low boiling azeotropic mixtures of water and solvent, retention of the polyhydric alcohols by the fibre, and others. It was thought desirable, therefore, to apply a procedure which makes possible direct dissolution of the dyes in the organic solvent. To achieve this, one can make use of the fact that ionic dyes often form a solvent-soluble complex with surface active agents of opposite charge. This procedure has been widely followed for analytical purposes (5) but has found limited application only in solvent dyeing (6,7). In this paper, some preliminary results are reported which have been obtained by solvent dyeing of wool with reactive dyes in the presence of both cationic surface-active agents and fibre-swelling agents such as water or ethylene glycol.

## EXPERIMENTAL

Untreated all-wool doctor flannel was used as the substrate and perchloroethylene was used as the solvent. Dye solutions were prepared by adding equal amounts of dye and hexadecylpyridinium chloride to the solvent and heating and stirring until a clear solution was obtained. The solution was then cooled to 60°C, 100 ml each placed in stainless steel capsules of 300 ml capacity, the required amounts of water or glycol added and 10 g samples of the fabric entered. The capsules were then placed in a Linitest apparatus, the temperature was increased by 1°C/min to 100°C, and dyeing continued at this temperature for 1 hour. The samples were then removed, rinsed in 80% aqueous ethanol to remove the solvent, and dried.

For comparison, aqueous dyeings were also carried out in a bath containing the dye, 4%  $(\text{NH}_4)_2\text{SO}_4$ , 1% Albegal B (Ciba-Geigy) and acetic acid to give a pH of 4.5. The liquor to goods ratio was 10:1. Dyeing was commenced at 50°C, the temperature increased at a rate of 1°C/min to 100°C and dyeing continued for 1 hour.

Exhaustion values of both the aqueous and the solvent dyeings were determined by spectrophotometric analysis of the exhausted liquor.

Covalent fixation values were determined by extraction of the dyed samples, after washing in ammonia solution<sup>(3)</sup>, with 20% aqueous pyridine at 100°C for 1 hour and spectrophotometric analysis of the extract. All percentages are given on mass of fabric (o.m.f.).

## RESULTS AND DISCUSSION

From the results listed in Table 1 it is apparent that little dye was taken up by the fibre from the pure dye/surfactant solution, because in this case the partition coefficient of the dye between solution and fibre was obviously very much in favour of the solution. Attempts to shift this partition coefficient in favour of the fibre were made in different ways: It was tried to increase the dissociation of the dye/surfactant complex by the use of surfactants with either a shorter alkyl chain length or of those with more hydrophilic residues at the quaternary nitrogen, such as the 2-hydroxy alkyl group. These indeed gave better exhaustion values, but at the same time produced very unlevel dyeings. It should be noted here that even with the hexadecylpyridinium chloride, high exhaustion values (in the absence of a wetting agent) were often accompanied by unlevelness.

Since a precipitation of the dye at the fibre surface rather than a penetration of the dye into the interior of the fibre seems to have occurred here, it was tried to modify the fibres, by application of a suitable fibre swelling agent, in such a way as to enable a proper dyeing reaction. From the va-

**TABLE I**  
**INFLUENCE OF % ETHYLENE GLYCOL ON EXHAUSTION AND COVALENT FIXATION VALUES OBTAINED FROM DYEING**  
**WITH 2% EACH OF DYE AND HEXADECYLPYRIDINIUM CHLORIDE**

DYE	% ETHYLENE GLYCOL	% EXHAUSTION	% COVALENT FIXATION
C.I. Reactive Blue 69	0	0	—
	2	10	95
	4	20	94
	6	26	93
	10	50	90
	15	68	89
	20	84	87
	40	85	85
	Aqueous dyeing	100	80
C.I. Reactive Blue 74	0	12	98
	2	16	96
	4	24	96
	6	32	94
	10	28	93
	15	64	89
	20	80	89
	40	80	89
	Aqueous dyeing	95	79
C.I. Reactive Red 104	0	50	94
	2	51	94
	4	53	89
	6	59	87
	10	60	81
	15	68	79
	20	78	78
	40	80	77
	Aqueous dyeing	78	74
C.I. Reactive Blue 29	0	39	97
	2	39	86
	4	39	90
	6	39	87
	10	55	85
	15	64	79
	20	74	80
	40	83	77
	Aqueous dyeing	100	68
C.I. Reactive Yellow 39	0	15	95
	2	29	94
	4	33	92
	6	33	87
	10	59	84
	15	85	80
	20	92	78
	40	92	78
	Aqueous dyeing	92	77

**TABLE III**  
**INFLUENCE OF % WATER ON EXHAUSTION AND COVALENT FIXATION VALUES OBTAINED FROM DYEING WITH 2% EACH**  
**OF DYE AND HEXADECYLPIRIDINIUM CHLORIDE**

DYE	% WATER	% EXHAUSTION	% COVALENT FIXATION
C.I. Reactive Red 84 (87°C)	0	10	—
	2	13	91
	4	35	—
	6	42	—
	10	38	—
	15	54	—
	20	65	81
	40	57	—
C.I. Reactive Red 84 (100°C)	0	2	—
	2	10	93
	4	15	—
	6	42	—
	10	72	—
	15	90	—
	20	93	88
	40	93	—
C.I. Reactive Red 91 (87°C)	0	40	—
	2	42	94
	4	40	—
	6	47	—
	10	57	—
	15	69	—
	20	72	85
	40	84	—
C.I. Reactive Blue 29 (100°C)	0	0	—
	2	0	—
	4	0	—
	6	5	—
	10	38	—
	15	79	—
	20	81	91
	40	81	—
C.I. Reactive Blue 27 (100°C)	0	18	—
	2	30	82
	4	45	—
	6	52	—
	10	71	—
	15	72	—
	20	71	77
	40	70	—
C.I. Reactive Yellow 39 (100°C)	0	12	—
	2	15	95
	4	44	—
	6	60	—
	10	88	—
	15	91	—
	20	96	86
	40	94	—

Addition of non-ionic compounds such as laurylmonoethanolamide had no effect at all. It was therefore decided to substitute the ethylene glycol by water, a method which has been successfully applied to the dyeing of wool with acid dyes by Nemoto *et al*<sup>(7)</sup>, who used long-chain aliphatic amines instead of the quaternary salt.

Some results obtained with this procedure are given in Table III. Part of these dyeings were carried out at a final temperature of 87 C, the boiling point of the azeotrope formed from water and perchloroethylene. Because it was found here that the covalent fixation values did not depend very much on the amount of water added, these values were determined only for 2% and 20% of water, respectively. From these results it can be seen that values for both exhaustion and covalent fixation compare well with those obtained with ethylene glycol, the fixation values sometimes being even higher. The effect of temperature can be derived from the two dyeings with the C.I. Reactive Red 84. With low amounts of water, the exhaustion is lower for the higher temperature, because there is always a certain quantity of water evaporated to saturate the space left above the liquid in the capsule. With sufficient water added, however, this is just reversed, the exhaustion now being remarkably higher at the higher temperature. As in the case of ethylene glycol, covalent fixation values were generally lower for the higher concentration of water, the possible reasons for this having been discussed earlier.

In the practical application of this process, the effect of temperature would call for the use of a pressurised dyeing apparatus. The most striking difference, however, between glycol and water is the degree of levelness, which was excellent in all cases by the use of water, even when carrying out mixed dyeings with three different dyes.

Little evidence has so far been obtained on the mechanism of the dyeing reaction and on the possible role of the glycol and water. Water certainly does not act as a solvent for the dye because no dyeing is obtained, with the amounts of water used in the present experiments, when the quaternary salt is omitted. The water, as well as the glycol, should then merely act as a swelling agent for the fibre thereby enabling diffusion of the dye into its interior to take place. One experimental result points in this direction: Samples of the fabric were equilibrated for 48 hours at 100% R.H. and then dyed from the solvent without further addition of water. Since the moisture regain is then about 35%<sup>(8)</sup>, another experiment was carried out whereby a dry sample was entered into the dye solution and then 35% of water o.m.f. added. Similar results were obtained from both experiments.

This could mean that the dye-surfactant complex breaks up into its components at the solvent-wet fibre-interface, and the dye ion then enters the fibre. In the case of the acid dye/aliphatic amine salts<sup>(7)</sup>, this dissociation obviously needs to be assisted by the addition of an anionic surfactant

such as dioctyl sodiumsulphosuccinate (DOSS), possibly according to the following reaction:

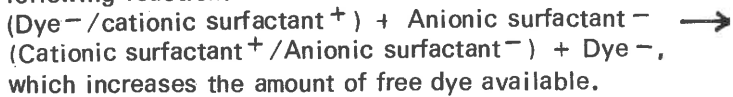


TABLE IV  
INFLUENCE OF % DOSS \* ON EXHAUSTION VALUES OBTAINED FROM DYEING WITH 2% EACH OF DYE AND HEXADECYLPYRIDINIUM CHLORIDE AND 20% OF WATER

DYE	% DOSS *	% EXHAUSTION
C.I. Reactive Red 84	0	86
	1	95
	2	95
	3	100
	4	100
	5	100
C.I. Reactive Blue 27	0	78
	1	85
	2	90
	3	100
	4	100
	5	100

\* DOSS = Dioctyl sodiumsulphosuccinate

To ascertain whether this is valid for reactive dyes too, some additional experiments were carried out where increasing amounts of DOSS were added to a dyebath containing 20% of water and 2% each of dye and hexadecylpyridinium chloride. Dyeing was carried out as described earlier at a final temperature of 100°C. From the results listed in Table IV it is evident that the addition of DOSS indeed increased the exhaustion. The effect was rather small, however, because exhaustion values were already high in the absence of DOSS. Moreover, with high amounts of DOSS, dyeings became unlevel due to precipitation of dye as discussed earlier, and a considerable amount of dye was washed out during the rinsing procedures.



Since the differences between the acid dye/amine salts and the reactive dye/cationic surfactant salt are possibly due to a greater stability of the former, it was tried to ascertain whether this is due to the properties of the dyes or to those of the cationic compounds. Reactive dye/amine salts were, therefore, prepared according to the method described by Nemoto *et al* (7), by precipitation of the dye from aqueous solution with the hydrochloride of 1-Aminohexadecane. The dye/amine salts so obtained were dissolved in perchloroethylene, different amounts of water and DOSS were added, and dyeings carried out as described for the dye/cationic surfactant system. The final temperature was always 100°C. The amount of 3% of the dye/amine salt applied here roughly corresponds to 2% of pure dye.

**TABLE V**  
**INFLUENCE OF % WATER ON EXHAUSTION VALUES OBTAINED FROM DYEING WITH 3% OF DYE/HEXADECYLAMINE SALT**

DYE	% WATER	% EXHAUSTION
C.I. Reactive Red 84	0	77
	5	77
	10	81
	20	87
	40	90
C.I. Reactive Blue 27	0	10
	5	31
	10	50
	20	63
	40	75

From the results listed in Table V it is evident that there was little difference between the dye/amine salt and the dye/pyridinium salt in the case of the blue dye, whereas with the red dye, exhaustion was remarkably higher for the dye/amine salt (e.g. Table III), especially with low amounts of water. This was, however, again accompanied by dye precipitation, as estimated from the amount of dye washed out during rinsing.

The effects of DOSS on dyeing with the dye/amine salt (Table VI) were similar to those obtained with the dye/pyridinium salt (Table IV). Since it was observed during these experiments that the hydrophobic character of the dye/surfactant complex – to which both its constituents contribute – and

hence its solubility in the organic solvent, plays a major role, this was compared qualitatively for a number of dyes. From these estimations it was revealed generally that:

1. the complexes of acid dyes were more soluble in perchloroethylene than those of reactive dyes, obviously due to a higher degree of sulphonation of the latter;
2. the complexes with the pyridinium salt were more soluble in perchloroethylene than those with the amine salt, due to the more hydrophobic character of the former;
3. in the specific case of the two dyes mentioned in Tables IV, V, and VI, the complexes of the blue dye were by far more soluble than those of the red dye.

**TABLE VI**  
**INFLUENCE OF % DOSS \* ON EXHAUSTION VALUES OBTAINED FROM DYEING WITH 3% OF DYE/HEXADECYLAMINE SALT IN THE PRESENCE OF 20% OF WATER**

DYE	% DOSS *	% EXHAUSTION
C.I. Reactive Red 84	0	81
	1	90
	2	84
	3	100
	4	100
C.I. Reactive Blue 27	0	50
	1	63
	2	68
	3	81
	4	87

\* DOSS = Dioctyl sodiumsulfosuccinate

From these observations and from the results of the dyeings one can draw the following conclusion: an equilibrium is set up at the fibre-solution interface determined quantitatively by the partition coefficient of the dye between the fibre and the solution. This partition coefficient can be increased, on the one hand, by the addition of increasing amounts of fibre-swelling agents like ethylene glycol or water, and on the other hand by either the application of dyes or cationic surfactants of a more hydrophilic

character or by the addition of anionic surface active agents. It is, however, not possible to compensate for very low amounts of fibre-swelling agents by any of the other measures mentioned above, because a very low solubility of the dye/surfactant complex leads to precipitation of the dye at the fibre surface. The dyeing rate is also decreased because the dye has to move through the solvent phase.

## SUMMARY AND CONCLUSIONS

It has been found that wool can be dyed successfully with reactive dyes from a solvent system by the use of the solvent-soluble complex of dye and a cationic surface active agent, if small amounts of water or ethylene glycol are added to the dyeing liquor. These compounds seem to act as fibre-swelling agents rather than as co-solvents for the dyestuff, but the amount of experimental material available at present is still too small as to enable the establishment of the mechanism of this new process.

The kinetics as well as the applicability of the process to bulk scale dyeing also remain to be verified.

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